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*Full Length Research Paper*

# Conversion of methanol to hydrocarbons on cobalt and lanthanum catalysts

**M. Riad* and S. Mikhail**

Egyptian Petroleum Research Institute, Nasr City, Hai Al-Zehour, P.O. Box 11727, Cairo, Egypt.

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**γ-Alumina supported cobalt (4 wt%) and cobalt-lanthanum with different lanthanum content (2,4 and 6 wt%) have been used as catalysts for methanol conversion. The catalysts were physically characterized using: X-ray diffraction technique, hydrogen temperature programmed reduction (TPR) and BET surface area measurements. The results established the formation of $Co_3O_4$ and $LaCoO_3$ oxide phases. The catalytic behavior of the prepared catalysts was investigated under atmospheric pressure in a pulse micro-reactor operating between 200 to 300°C and a nitrogen carrier gas flow 50 ml/min. The hydrocarbon-converted products discriminate the role of the different formed oxide phases of cobalt and lanthanum on the catalytic behavior of methanol conversion.**

**Keywords**: Methanol, alumina, cobalt, lanthanum, catalysts, hydrocarbons.

## INTRODUCTION

The most important route for the conversion of methanol is via either a mixture of CO and $H_2$ known by synthesis gas which is formed by steam reforming of natural gas or gasification of coal or from biomass. Methanol is available in abundance therefore it has been used as a raw material for the production of gasoline and olefins.

Leonardo et al. (2008) study the conversion of methanol into gasoline using molecular sieve SAPO-34 with high density of strong acid sites (Karge et al., 1994). Morten et al. (2008) investigate the performance of zeolite in the conversion of methanol to gasoline. Extensive literature was also concerning on conversion of methanol to hydrocarbon over zeolite catalyst for the formation of light alkenes (Chang and Silvestri, 1977; Vora et al., 1997; Yurchak, 1988; Hutchings et al., 1990, 1994).

Mikhail et al. (1996), (1991) studied the catalytic conversion of ethanol to hydrocarbon using H-faujsite zeolite and H-mordenite as catalysts. At lower reaction temperature range 300 to 375°C, ethanol partially dehydrated to ethylene, while at high temperature 400 to 450°C, the converted products consist of paraffinic gases and aromatics. Low space velocity resulted in high selectivity for aromatic but at high space velocity, the hydrocarbons gaseous predominate.

Freeman et al. (2002) also investigated this reaction over $Ga_2O_3$/HZSM and $Ga_2O_3$-$WO_3$/alumina catalysts at 400°C and found that the addition of $Ga_2O_3$ to HZSM increases the selectivity to aromatics at the expense of $C_2$-$C_4$ hydrocarbons. Meanwhile, its addition to $WO_3$/alumina increases the selectivity to methane.

The aim of this work is to prepare cobalt, lanthanum and cobalt- lanthanum /γ-alumina catalysts with different lanthanum loading (2, 4 and 6 wt%) and study the nature of the catalytic active sites and their role in the activity and selectivity control of methanol conversion to hydrocarbons.

## EXPERIMENTAL

### Catalysts preparation

Aluminum hydroxide supplied from Naga - Hammadie Aluminum-Company was calcined at 450°C to produce γ-alumina-supported material. The prepared catalysts were;

Cobalt (4 wt% based on the weight of alumina support)/ γ-alumina
Lanthanum (4 wt%)/ γ-alumina
Cobalt (4 wt%) – Lanthanum (2 wt%)/ γ-alumina
Cobalt (4 wt%) – Lanthanum (4 wt%)/ γ-alumina
Cobalt (4 wt%) – Lanthanum (6 wt%)/ γ-alumina

The catalysts were prepared by successive wet impregnation technique of γ-alumina support with the corresponding chloride

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*Corresponding author. E-mail: maryriad2006@yahoo.com.

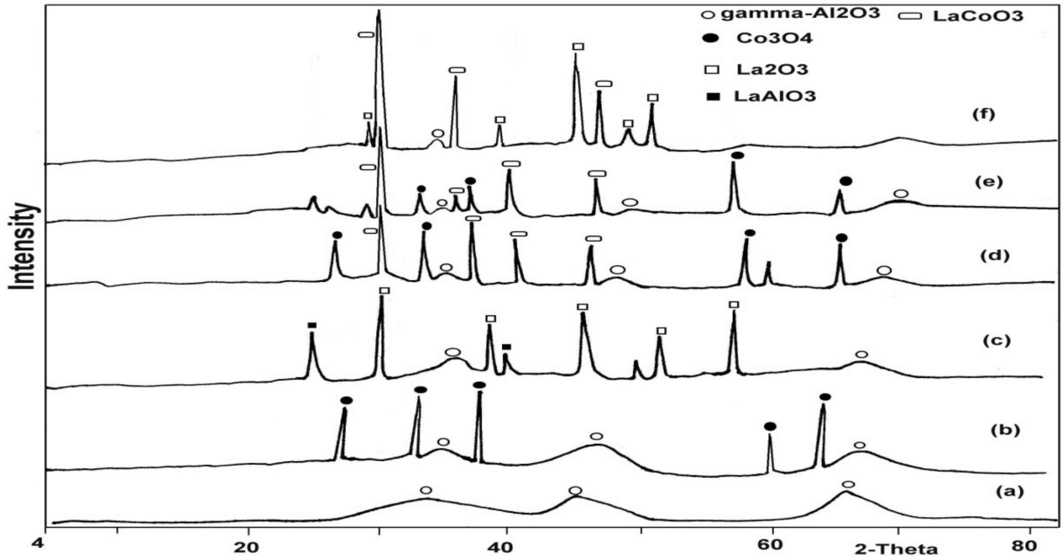

**Figure 1.** X-ray Diffraction Pattern for: (a) γ-alumina (b) Co/alumina (c) La/alumina (d) Co-La(2%)/alumina (e) Co-La (4%)/alumina (f) Co-La (6%)/alumina Catalysts.

solutions of cobalt and lanthanum. The prepared catalyst materials were dried at 120°C and then calcined in presence of flow of purified air at 600°C for six hours.

### Structural phase changes

The prepared catalysts were characterized by applying different techniques.

### X- ray diffraction pattern (XRD)

X-ray powder diffraction was carried out using XD-D1 – x-ray diffraction Schimadzu apparatus to detect the formed crystalline phases, CuKα radiation was the light source with applied voltage of 40 V and current of 40 mA. Two theta angles ranged from 4 to 80° with speed of 2° per min.

### Temperature-programmed reduction (TPR)

Was carried out using a Micromeritics CHEMBET-3000 TPR/TPD apparatus. The catalysts were firstly heated in a flow of $N_2$ (at 500°C) for one hour and then cooled to the room temperature. Then, the catalysts were reduced in a mixture of 10% hydrogen in nitrogen with flow rate 55 cm$^3$ min$^{-1}$, at increasing temperature programmed to a rate of 10°C/min up to 1000°C. Catalyst weight used for TPR measurements was about 0.1 g.

### Surface acidity

A Boehm's base neutralization technique, Boehm (1966) was used for measuring the surface acidity of the prepared catalysts. In this technique, 2.5 g of sample was mixed with 100 ml of 0.1 N NaOH solution and maintained overnight at room temperature. The mixture was left to settle and then filtered. The excess sodium hydroxide was titrated with standard 0.1 N HCl solution. The alkali neutralizes the acidic groups and therefore measures the total surface acidity of the prepared catalysts.

### Nitrogen physisorption isotherms

They were measured using quanta-chrome nova-automated gas sorption apparatus. The sample was out-gassed at 300°C (10 to 4 Pa), surface area was calculated from adsorption curve by BET method.

### Catalytic activity

The catalytic conversion of methanol is carried out in a pulse micro-reactor constructed by modifying a gas chromatographic assembly by the introduction of a stainless steel tube between the sample inlet and the analytical column.

The activities of the studied catalysts are measured by carrying out the methanol conversion reaction at temperature range of 250 to 300°C under atmospheric pressure. Each experiment used 0.5 g of dried material held in place by glass wool. Nitrogen (with rate 50 ml/min.) was chosen as the carrier gas because unlike hydrogen, it would not react with the intermediate products. A 2 µl pulse of the reactant is injected into the reactor bed through a septum near the reactor inlet. The reaction outputs were immediately analyzed by flame ionization detector (FID) through a chromatographic column packed with chromosorb b 80 to 100 mesh size and loaded with 20% by weight silicon oil-550.

## RESULTS AND DISSCUSSION

### X-ray Diffraction Pattern

X-ray diffraction patterns (XRD) for the support and the studied catalysts are shown in Figure 1(a-f). Diffractogram for the support material (Figure 1a), shows peaks at

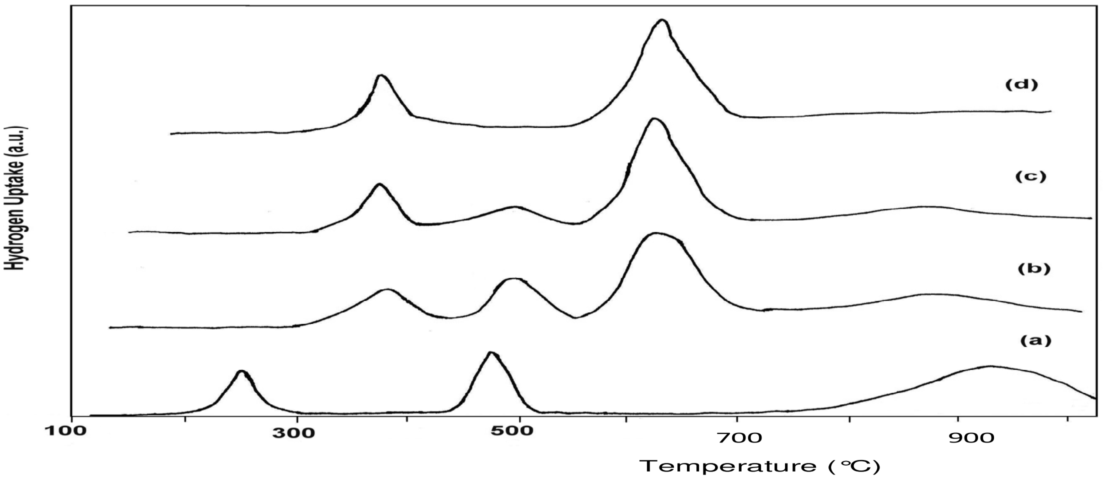

**Figure 2.** Temperature Programmed Reduction for: (a) Co/alumina, (b) Co-La(2%)/alumina, (c) Co-La (4%)/alumina and (d) Co-La (6%)/alumina Catalysts.

diffraction angles: 2θ = 37.3, 45.7 and 66.4°, which were typical of γ-alumina (Fraga et al., 2004). For cobalt/ alumina catalyst, the pattern shows peaks at 2θ = 31.3, 37.2, 44.8 and 59.8° which characterize the mixed cobaltous - cobaltic oxide $Co_3O_4$ as confirmed by Liotta et al. (2004) in addition to lines characterize γ-alumina.

For lanthanum/γ-alumina catalyst, the pattern shows lines at 2θ = 25.5, 39 and 56.6° that characterize $La_2O_3$ phase, in agreement with (Fraga et al., 2004) investigation. In addition, lines detected at 2θ = 24.3, 34.2 and 41° that is related to $LaAlO_3$ species, lines characterize γ-alumina are still detected.

For Co-La (2%)/γ-alumina catalyst, new diffraction lines appeared at 2θ = 33.2, 40.6, 47.5 and 59.2° which characterize the $LaCoO_3$ phase, as detected by Ji et al. (1996) in addition to lines characterize the $Co_3O_4$ species. No lines are detected for $La_2O_3$ species.

For Co-La (4%)/ γ-alumina catalyst, the intensities of lines characterize the $LaCoO_3$ phase was increased, meanwhile the intensities of $Co_3O_4$ characteristics lines decreased, compared with Co-La (2%)/ γ-alumina catalyst.

For Co-La (6%)/γ-alumina catalyst, $Co_3O_4$ diffraction lines are completely disappeared, whereas lines characterize $La_2O_3$ are observed.

Moreover, the detection of γ-alumina lines via XRD after the thermal treatment of prepared catalyst at 600°C is an indication for the thermal stability of γ-alumina that transformed to other transition phase's (either δ-, θ-, α-alumina) above 450°C. It is well known that, the transformation of γ-alumina into other phases is based on the reaction between the anionic vacancies that are presented due to the defective intrinsic character of the alumina structure. Therefore, when an alumina is doped with a cation that has ionic radius similar to that of $Al^{3+}$ ions like $La^{3+}$ may be incorporated in the spinel lattice in the vacancies and consequently hindering the formation of α-alumina. The thermal stability of alumina is also due to the fact that, the incorporated metal cations either La or Co interact with the alumina hydroxyl groups as a consequence, the generation of anionic vacancies along the dehydroxylation step would hindered and then improving the support stability (Morterra et al., 1996).

## Crystallite size

Average crystallite size is calculated using Scherer's formula from the pattern resolved peaks for $Co_3O_4$, $La_2O_3$ and $LaCoO_3$ species.

The crystallite size for $Co_3O_4$ species in Co/ γ-alumina catalyst is shown to be greater value 26.0 than that for $La_2O_3$ in lanthanum catalyst, 18.5 nm. Meanwhile, the interaction of cobalt and lanthanum resulted in the formation of much smaller crystallite $LaCoO_3$ species (16.6 nm), which is in agreement with the results obtained by Zhang et al. (2005). The increase in lanthanum loading from 2 to 4 to then to 6 wt% causes a decrease in the crystallite size of $LaCoO_3$ species from 16.6 to 11.6 then to 8.6 nm. This behavior is due to the chance for the presence of free bulk oxide $Co_3O_4$ is decreased with the appearance of small crystallites $La_2O_3$ (as verified by XRD data) which help in the dispersion of $LaCoO_3$ species, preventing their aggregation.

## Temperature programmed reduction

Temperature programmed reduction (TPR) profiles for the studied catalysts are shown in Figures 2a to 2d. TPR profile for cobalt catalyst (Figure 2a) reveals two hydrogen consumption peaks at 250 and 425°C, the first peak

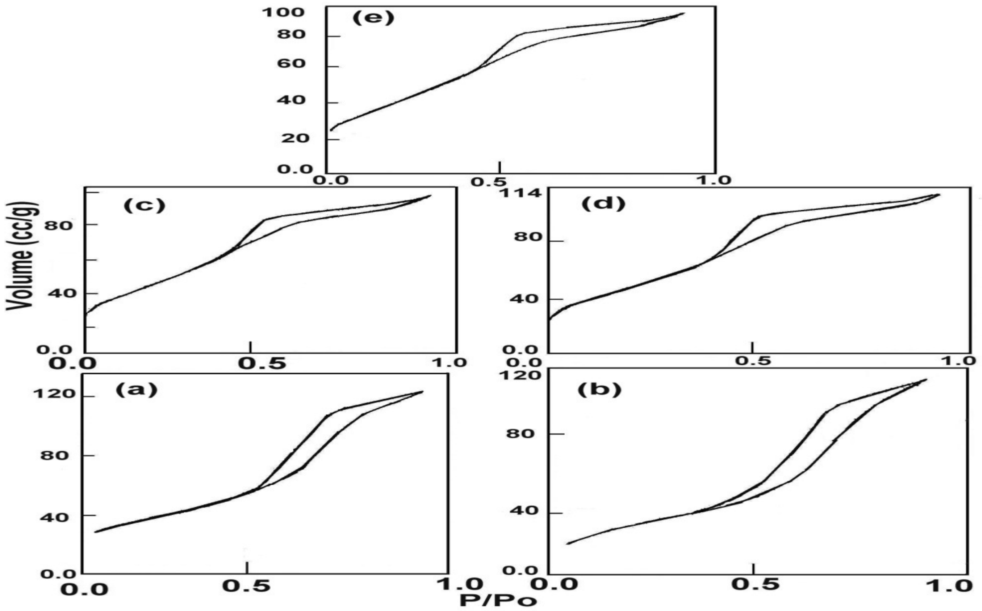

**Figure 3.** $N_2$-Adsorption-Desorption Isotherms for: (a) Co/alumina, (b) La/alumina (c)Co-La2%/alumina, (d)Co-La4%/alumina and (e) Co-La 6%/alumina catalysts.

is related to the reduction of $Co^{3+}$ to $Co^{2+}$ of $Co_3O_4$ phase and the one with high temperature is due to the reduction of $Co^{2+}$ to $Co^{o}$ of $Co_3O_4$ phase (Vofi et al., 2002; Venezia et al., 2007). In addition, reduction peak at -900°C, that attributed to the reduction of cobalt species strongly interacting with alumina (Li et al., 2001). For Co-La (2%)/γ-alumina catalyst (Figure 2b), new reduction peaks are appeared at 390 and 640°C, in addition to cobalt reduction peak which shifted to higher temperature at 495°C. Since lanthanum is non-reducible under the TPR condition so TPR peaks probable belonged to the reduction of cobalt species (Lago et al., 1997).

Navarro et al. (2007) reported that $LaCoO_3$ phase showed TPR peaks at 360 and 610°C corresponding to the reduction of $Co^{3+}$ to $Co^{2+}$ then to Co°. Hence, the TPR peaks at 390 and 640°C related to the reduction of $Co^{3+}$ to $Co^{2+}$ and to Co° in $LaCoO_3$ phase.

Navarro et al. (2007) also reported the mechanism for the reduction of $Co^{3+}$ in $LaCoO_3$ that occurs as follow:

$$2LaCoO_3 + H_2 \rightarrow 2LaCoO_{2.5} + H_2O$$
$$2LaCoO_{2.5} + 2H_2 \rightarrow La_2O_3 + 2Co^{o} + 2H_2$$

Thus, the two separate peaks arise in TPR profile around 390 and 640°C were assigned to consecutive reduction of $Co^{3+}$ to $Co^{2+}$ in $LaCoO_{2.5}$ and to Co° finely dispersed on $La_2O_3$ species.

Moreover, the area of $Co_3O_4$ reduction peak at 495°C is decreased upon increasing lanthanum loading and disappeared at "6% lanthanum loading" indicates the prevailing of $LaCoO_3$ phase and disappearance of $Co_3O_4$ species in Co-La (6%)/γ-alumina catalyst.

## Surface acidity

The surface acidity of the calcined catalysts was measured according to Boehm's (1966) technique who concluded that the alkali neutralize the acidic groups and therefore measure the total surface acidity of the studied catalysts.

Upon the interaction of cobalt with alumina, the acidity increased from 22.0 (for γ-alumina) to 26.0 $meq.g^{-1}$, due to the acidic properties of cobalt species. Meanwhile it decreases to 20.7 $meq.g^{-1}$ upon the interaction of alumina with lanthanum species, where $La_2O_3$ is characterized by its basic properties. For La-Co (2%)/ γ-alumina catalyst, the surface acidity is increased to 28.9 $meq.g^{-1}$. In addition, the increase of lanthanum loading from 2 to 4 then to 6 wt% causes an increase in surface acidity from 28.9 to 30.0 then to 30.7 $meq.g^{-1}$, in agreement with Navarro et al. (2007) investigation who observed that, the high acidity of $LaCoO_3$ species is due to the presence of large number of structural defects (Lewis acid sites).

## Surface properties

Nitrogen isotherms were measured using "quanta-chrome nova automated gas sorption apparatus". Full nitrogen adsorption-desorption isotherms were obtained for the studied catalysts (Figures 3a to 3e). The data for surface properties, specific surface area ($S_{BET}$), total pore volume ($V_p$) and mean pore radius ($r_H$), were included in Table 1.

**Table 1.** Surface properties of the studied catalysts.

| Catalyst | $S_{BET}$ ($m^2/g$) | $r_H$ (nm) | $V_p$(cc/g) |
|---|---|---|---|
| Alumina | 170.8 | 11.0 | 0.125 |
| Cobalt | 82.0 | 12.8 | 0.05 |
| Lanthanum | 103.6 | 8.0 | 0.042 |
| Co-La2% | 155.3 | 8.0 | 0.063 |
| Co-La4% | 161.6 | 8.0 | 0.066 |
| Co-La6% | 166.0 | 8.0 | 0.068 |

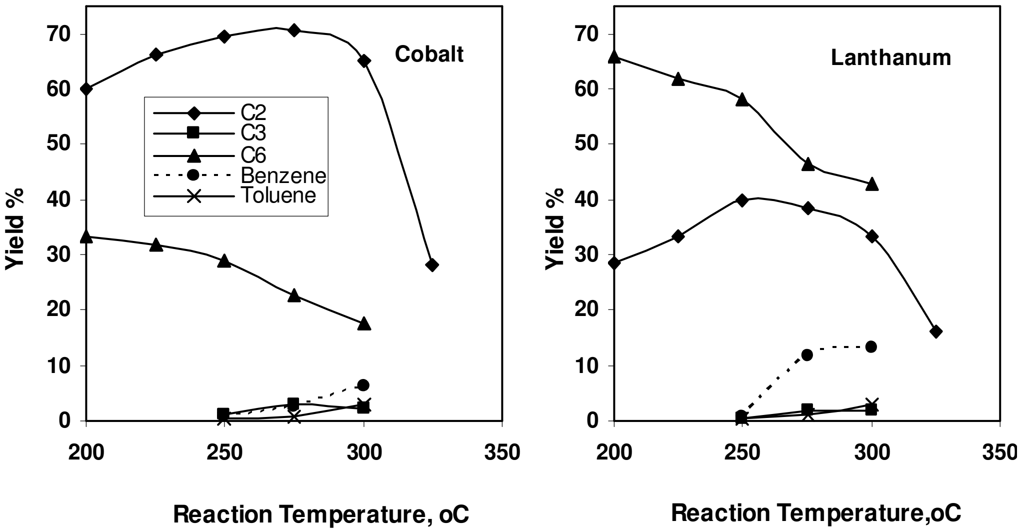

**Figure 4.** Conversion Products of Methanol on Co and La/ γ-alumina Catalysts.

All samples showed type IV isotherm of Brunauer et al. classification (1940) according to IUPAC classification, cobalt and lanthanum catalysts exhibited H1 hysteresis loop which often obtained with agglomerates or compacts spheroidal particles of fairly uniform size and array, meanwhile Co-La catalysts with different lanthanum loading exhibited H2 hysteresis loop. This kind of hysteresis loop was an indication for a network of interconnected pores with narrower parts (Figure 3). Thus, the interaction of cobalt with lanthanum on alumina support causes a modification in the texture structure compared with monometallic counterpart catalyst.

The $S_{BET}$ values for the calcined catalysts were computed from linear plots of the $S_{BET}$ equation. Data in table indicates that, the surface area of alumina decreased upon loading with either cobalt or lanthanum and a decrease in pore volume is observed. This decrement may be due to bulk crystallites $Co_3O_4$ species blocking some narrow pores and in accordance new wide pores are formed, (as indicated from the increase in average pore radius) which responsible for the noticeable decrease in surface area from 170.8 for γ-alumina to 82.0 $m^2/g$ for Co/ γ-alumina catalyst.

Meanwhile, the loading with lanthanum show lower surface area losses (103.6 $m^2/g$) compared with cobalt catalyst (Table 1). Meanwhile, the decrease in average pore radius upon lanthanum loading may be due to the formed $La_2O_3$ species that create some narrow pores that accompanied also with a decrease in pore volume.

Concurrently, the incorporation of La (2%) species to cobalt catalyst shows a noticeable increase in surface area (155.0 $m^2/g$) in comparison with La catalyst. Also, as lanthanum loading increases from 2 to 4 then to 6%, the surface area increases from 155.0 to 161.6 then to 166.0 $m^2/g$ (Table 1). This reflects the contribution of $La_2O_3$ species in the dispersion of the formed oxide phases and the creation of some narrow pores results in the observed increase in surface area.

## Catalytic activity

The catalytic conversion of methanol was studied at reaction temperature range of 200 to 300°C and the data are represented in Figures 4 to 6. On using the monometallic Co and La/ γ-aluminacatalysts, the main reaction

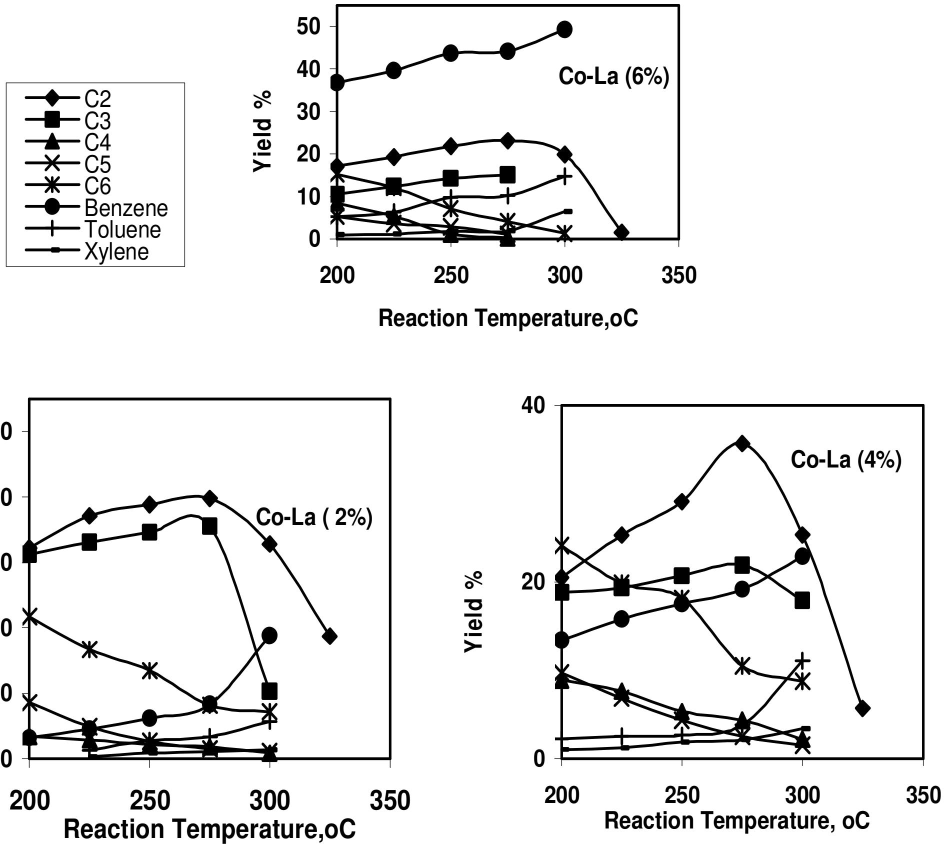

**Figure 5.** Conversion Products of Methanol on Co-La catalysts using Different Lanthanum Loading.

products consisted of ethane, propane and hexane at all reaction temperatures, benzene and toluene start to appear at reaction temperature 250°C, besides xylene that appeared as traces at 300°C. As the reaction temperature increases the yield of ethane and propane increases and show maximum values at reaction temperature 275°C (70.6 and 2.8%) for Co/γ-alumina catalyst and at reaction temperature 250°C (38.5 and 2.0%) on using La/ γ-alumina catalyst (Figure 4).

On the other hand, the yield of hexane hydrocarbons at all reaction temperatures is higher on using lanthanum catalyst than on cobalt one. Benzene and toluene aromatic hydrocarbons appear as traces at reaction temperature 250°C and continuously increase with the increase in reaction temperature up to 300°C (Figure 4). Meanwhile, the yield of hexane hydrocarbons decreases with the increase in reaction temperature. The same trend is observed for aromatic products, which show higher yield on using La catalyst. This is an indication that: lanthanum active sites prefer the formation of aromatic compounds. Meanwhile, $Co_3O_4$ species preferred the cracking reaction, in agreement with Desai and Richardson (1986) conclusion and as established from the higher yield of $C_2$ alkane hydrocarbons, compared with lanthanum catalyst.

For bimetallic Co-La (2%)/ γ-alumina catalyst (Figure 5), the reaction products are mainly consisted of paraffinic (ethane, propane, butane, pentane, hexane) hydrocarbons with a maximum at reaction temperature 275°C and aromatic hydrocarbons benzene appeared at 200°C, toluene and xylene appeared at 225°C.

Benzene is the predominant aromatic product and their yields increases with the increase in reaction temperature. The increase in the yield of ethane and propane up to reaction temperature 275°C may have resulted from the cracking reaction as indicated from the simultaneous decrease in the yield of butane, pentane and hexane hydrocarbons.

The conversion reaction of methanol shows the same behavior upon increasing the lanthanum loading from 2 to 4 then to 6% (Figure 5) but with some differences which are:

i.) The yield of ethane and propane hydrocarbons decreases with the increase in lanthanum loading from 2 to 6%.

ii.) Toluene and xylene aromatic products start to appear at a reaction temperature of 200°C and the yield of aromatic hydrocarbon products increases continuously with the increase in reaction temperature and with lanthanum

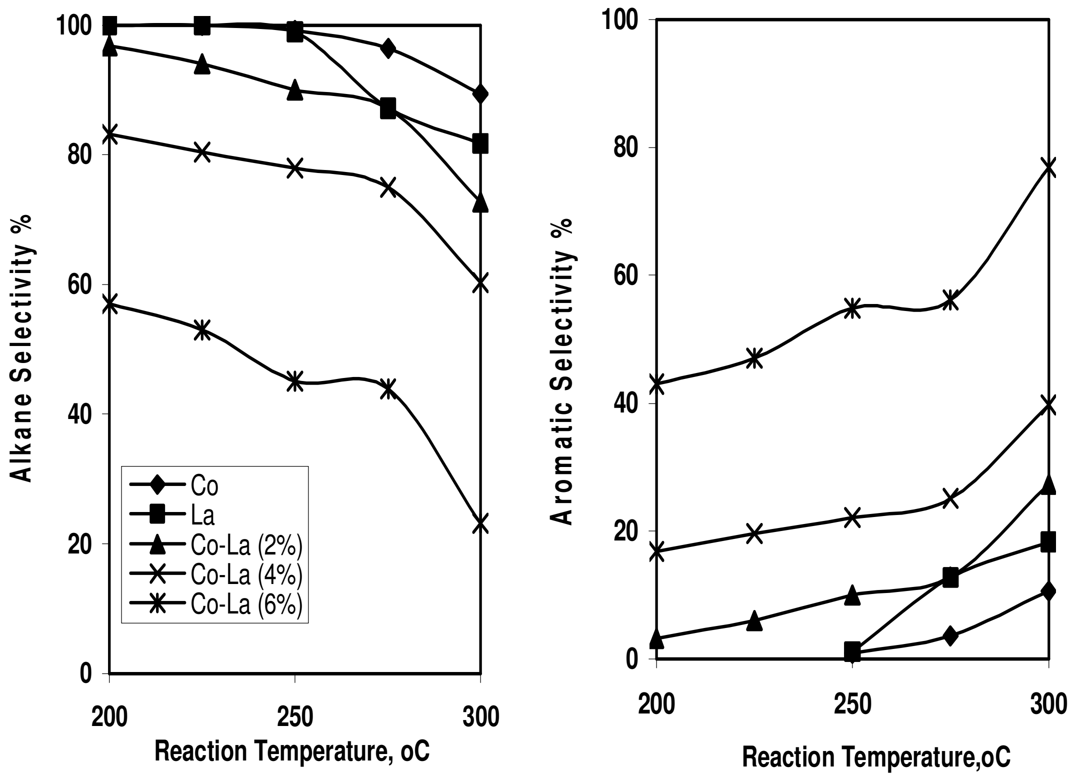

**Figure 6.** Selectivity % for Alkane and Aromatic Hydrocarbons Using the Prepared Catalysts.

loading.

iii.) The selectivity (S%) for alkane hydrocarbons formation decreases with the increase in the reaction temperature on using all the studied catalysts. It decreases from 72.7 to 60.0 then to 23.0% with the increase in lanthanum loading from 2 to 4 then to 6% respectively, at reaction temperature 300°C (Figure 6). Thus, Co-La (2%)/ γ-alumina catalyst is the most selective one for alkane formation.

iv.) The selectivity to aromatic hydrocarbons increases with the increase in the reaction temperature up to 300°C, and also it increases from 27.0 to 39.7 and then to 76.9%, on increasing La loading from 2 to 4 then to 6% (Figure 6). In other word, higher temperature and lanthanum loading prefer the formation of aromatic products. Co-La (6%)/ γ-alumina catalyst is the most selective one for aromatics formation.

## Reaction mechanism

It is well known that, the mechanism of transformation of methanol to hydrocarbons occurs through the formation of "oxonium" ion (via methoxy species and dimethyl ether) on the acidic acid sites of the prepared catalysts that induce a series of reactions leading to the formation of primary olfinic products (Asher et al., 1984) as followed:

$$2\,CH_3OH + H^+ \rightarrow CH_3OCH_3 + H_2O + H^+$$

$$CH_3OCH_3 + H^+ \rightarrow CH_3OH + CH_3{}^+$$

$$CH_3OCH_3 + CH_3{}^+ \rightarrow CH_3OH + CH_3CH_2{}^+$$

$$CH_3CH_2{}^+ \rightarrow CH_2{=}CH_2 + H^+$$

Moreover, the reaction continues to give higher olfinic products via repeated methylation, oligomerization and cracking of higher alkenes.

Light olefins are subsequently reacting further to form a mixture of paraffin, and aromatic hydrocarbons. The formation of aromatics from short chain alkene involves the following successive steps:

i. Oligomerization
ii. Formation of dienes through hydrogen transfer from oligomers to light alkenes
iii. Cyclization of diene into $C_5$ or $C_6$ cyclic olefins (whose inter isomerization is rapid)
iv. Hydrogen transfer from the cyclic to light alkenes

Moreover, the first benzenic molecules can be rapidly alkylated by methanol, (Schulz et al., 1991). The hydride transfer process leads to the disproportionation of alkene into alkanes and aromatic compounds. Indeed the formation of one molecule of aromatic hydrocarbon requires elimination through hydrogen transfer of six hydrogen atoms with the consequent formation of three alkane molecules.

Based on the physico-chemical characteristic of the prepared catalysts and the mechanism of methanol conversion reaction, the high yield and selectivity of aromatics formation on using Co-La (6%)/γ-alumina catalyst can be explained according to:

i. The surface properties informed the high surface area of Co-La (6%)/alumina catalyst compared by the other prepared catalysts. The increase in catalyst surface area that provided a high dispersion of $LaCoO_3$ and $La_2O_3$ species on alumina support thereby provide more acid (γ-alumina) and active sites for methanol conversion reaction.
ii. X-ray diffraction pattern and temperature programmed reduction detected the presence of $La_2O_3$ and $LaCoO_3$ species which form new sites catalyze secondary reaction of products formed initially by the acid sites of alumina.

$La^{+3}$ cations in $La_2O_3$ activate C-H bond which enhance donation of hydride species from methanol to surface methoxy intermediate in addition to its basic properties which facilitate the dehydroaromatization step (as seen from the higher yield of aromatic hydrocarbons). Then, the active sites can be considered $LaCoO_3$ in close proximity with free $La_2O_3$ and the acid sites of alumina. At these sites, it is probable that the activation and dimerization of the alkenes occur.

## Conclusion

In conclusion, the conversion of methanol on cobalt-lanthanum catalysts leads to formation of ethane, propane, butane, pentane, hexane alkane hydrocarbons, benzene, toluene and xylene aromatic hydrocarbons. The conversion of methanol to aromatics increases as the lanthanum loading increases, which indicate that the active sites necessary for formation of aromatics is $LaCoO_3$ and $La_2O_3$ in vicinity with γ-alumina acid sites that facilitate the formation of aromatics compounds.

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